

## PATENT ABSTRACTS OF JAPAN

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(54) CURABLE RESIN COMPOSITION, VARNISH AND PRINTING INK USING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a curable resin composition excellent in normal-temperature dryability, enabling high-speed printing therewith, and capable of giving printing ink excellent in trouble-proofing performance such as preventing set-off, comprising a drying oil, an active oxygen generator and resin(s).

SOLUTION: This composition comprises (A) a drying oil, (B) an active oxygen generator [pref. a compound having performance to generate singlet oxygen when irradiated with active rays, esp. a triplet sensitizer (e.g. benzophenone derivative)] and (C) resin(s) solid at normal temperatures (pref. at least one kind selected from the group consisting of modified phenolic resin, alkyd resin and petroleum resin), and pref. furthermore (D) a drier (desiccant).

*Cited document 2**(D2)*

[Claim(s)]

[Claim 1]A hardenability resin composition consisting of solid resin (C) at drying oil (A), an active oxygen generating agent (B), and ordinary temperature.

[Claim 2]A hardenability resin composition of \*\*\*\*\*I\*\*, wherein active oxygen which an active oxygen generating agent (B) generates is singlet oxygen.

[Claim 3]The hardenability resin composition according to claim 1, wherein an active oxygen generating agent (B) is a triplet sensitizer.

[Claim 4]The hardenability resin composition according to claim 1 characterized by a thing for which solid resin (C) is chosen from a group which consists of modified phenol resin, alkyl resin, and petroleum resin at ordinary temperature, and which is a kind at least.

[Claim 5]A hardenability resin composition which blends a dryer (D) with a hardenability resin composition given in Claims 1-4 further, and is characterized by things.

[Claim 6]A varnish which carries out dissolution mixing of the hardenability resin composition given in Claims 1-5 at a solvent (E), and is characterized by things.

[Claim 7]Printer's ink which carries out dispersion mixing of the paints (F) to the varnish according to claim 6, and is characterized by things.

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the hardenability resin composition excellent in ordinary temperature drying property, a varnish, and printer's ink using it as a vehicle in more detail about the printer's ink which used a hardenability resin composition, a varnish, and it.

[0002]

[Description of the Prior Art] In recent years, in printer's ink, printer's ink excellent in drying property is called for with improvement in the speed of a printing machine. However, in the printer's ink of the oxidative polymerization nature which uses conventional drying oil. Since the dry mechanism used the natural oxidation reaction of the carbon-carbon unsaturated bond in a drying oil molecule or a rosin molecule by oxygen of a ground state, it was pointed out that oxidation and crosslinking reaction speed are slow, and the drying property (what is called setting time) is insufficient.

[0003] Therefore, adding a dryer as a dryer is usually made that the drying property (set) of printer's ink should be improved. As such a drier, metal salt of organic carboxylic acid, such as naphthenic acid, octylic acid, and neo decanoic acid. For example, calcium, cobalt, lead, iron, manganese, zinc, zirconium salt, etc. are known, and in order to promote the printer's ink surface and internal hardening, these plurality is used, mixing suitably. However, promotion of oxidative polymerization with these dryers is the operation as a reaction accelerator which generally disassembles the oxide generated by the oxidation reaction by the oxygen molecule of a ground state. As an accelerator of the oxidation reaction by oxygen, it is insufficient. Then, the ink which brought oxidation reaction of drying oil forward further, and was excellent also in preservability has been needed.

[0004] On the other hand, by using an ultraviolet curing type vehicle, the ultraviolet curing type printer's ink which hardens and constructs a bridge under UV irradiation for a short time is developed, and practical use is presented. However, in these ultraviolet curing inks, although the drying property in a short time became possible, therefore bridge construction and a polymerization reaction arise for a short time, it was easy to produce hardening distortion and SUBJECT, such as survival of the poor adhesion to a substrate or an unreacted low molecule thing, has arisen.

[0005]

[Problem(s) to be Solved by the invention] Therefore, the purpose of this invention makes oxidation reaction promote by using active oxygen excellent in the oxidation reaction nature of a carbon-carbon unsaturated bond. It is in providing printer's ink excellent in the trouble-proof performances which raise the drying property of ink remarkably, and make high-speed printing possible as the result, and are produced by dry [ poor ]. such as a set-off, the reverse side, sticking, blocking, and migration.

[0006]

[Means For Solving the Problem] This invention persons resulted in this invention, as a result of repeating research wholeheartedly that it should solve in consideration of many above problems. Namely, this invention is a hardenability resin composition first characterized by consisting of solid resin (C) at drying oil (A), an active oxygen generating agent (B), and ordinary temperature,

Subsequently, it is a hardenability resin composition which adds a dryer to this hardenability resin composition, is the varnish which carried out dissolution mixing of these hardenability resin composition with a solvent, and also is the printer's ink which carried out dispersion mixing of the paints to this varnish. [0007]

[Embodiment of the Invention] Hereafter, this invention is explained extensively. First, as drying oil (A) used by this invention, The ester compound which has at least one or more carbon-carbon double bonds in intramolecular is shown, the number of carbon atoms -- 3-25 -- and the unsaturated acid (for example, acrylic acid.) which has at least one or more double bonds Estene acid, hexene acid, octenate, dodecenoic acid, ricinoleic acid, oleic acid, linolic acid, linolenic acid, and eleostearic acid, the polyhydric alcohol (for example, alkyl diol, such as hexandiol,.) which has at least two or more hydroxyls Glycols, such as ethylene glycol and propylene glycol, glycerin, Ester compounds, such as trimethylolpropane, pentaerythritol, and dipentaerythritol, synthetic fatty oil which is ester compounds with the mixture of the above-mentioned unsaturated acid and saturated acid further, or a natural fat oil can be mentioned. A typical compound as a natural fat oil China wood oil, the linseed oil, soybean oil, The linseed-oil stand oil which safflower oil, tung oil, etc. were mentioned, in addition polymerized the linseed oil, The maleinized oil produced by denaturalizing by a maleic anhydride in drying castor oil and fatty oil (for example, tung oil) which are produced by drying castor oil, Synthetic drying oil, such as styrenated oil (or vinyltoluene-ized oil) produced by carrying out copolymerization to said drying oil and styrene (or vinyltoluene etc.), etc. can be illustrated.

[0008] Next, as an active oxygen generating agent (B) used by this invention, if it is a compound which has the performance which generates singlet oxygen by the exposure of actinic rays, there will be no limitation in particular, but, If has the optical absorption nature of ultraviolet (200 nm) - a near-infrared (900 nm) field, and the compound whose those with 155 or more kJ/mol and system intersection efficiency triplet energy level is at least 0.01 or more is used suitably. As an example of such a sensitizer (B), a naphthalene derivative, an anthracene derivative, A phenanthrene derivative, a pyrene derivative, a naphthacene derivative, a perylene derivative, Condensed multi-ring aromatic derivatives, such as a pentacene derivative, an acridine derivative, a benzothiazole derivative, The unsaturated ketone represented by a chalcone derivative, dibenzal acetone, etc. 1, 2-diketone derivative which are represented by benzyl, camphor quinone, etc., A benzophenone derivative, a benzoin derivative, a fluorene derivative, a naphthoquinone derivative, An anthraquinone derivative, a xanthene derivative, a thioxanthene derivative, A xanthone derivative, a thioxanthone derivative, a coumarin derivative, a keto coumarin derivative, Poly methine coloring matter, such as a cyanine derivative, a merocyanine derivative, and an oxo Nord derivative, An acridine derivative, an azine derivative, a thiazine derivative, an oxazine derivative, An indoline derivative, an azulene derivative, an AZURENIUM derivative, a squarylium derivative, A porphyrin derivative, a tetraphenyl porphyrin derivative, a triallyl methane derivative, a tetra benzoporphyrin derivative, a tetrapyrrazino porphyrine derivative, a phthalocyanine derivative, a tetraaza porphyrine derivative, A tetra amino KISARTO porphyrine derivative, a naphthalocyanine derivative, A sub phthalocyanine derivative, a pyrylium derivative, a thio

pyrylium derivative, the Iket Hafi Lyone derivative, an acoulene derivative, a spiro pyran derivative, a spiro oxazine derivative, A thiospiro pyran derivative, a metal arene complex, an organic ruthenium complex, etc. are raised. In addition, they are still more specifically a volume for big river NARASHIN, and a "coloring matter handbook" (in 1986.). The volumes for Kodensha and Shin Gswars, "the chemicals of functional dye" (1991, CMC), it is not what is limited to these although the coloring matter and the sensitizer of a description are raised to the volumes on Tadashi Ikemori 3 \*\*, and "special function material" (1986, CMC), in addition, coloring matter and the sensitizer which show absorption to the light applied to a near-infrared region are raised from ultraviolet, and two or more sorts of these may be used by arbitrary ratios if needed.

[0009]As a compound suitably used especially in this invention, For example, the triplet sensitizer which has absorption can be mentioned to ultraviolet regions, such as a benzophenone derivative, an acetophenone derivative, a xanthone (thio) derivative, a xanthone derivative (thio), a coumarin derivative, and a keto coumarin derivative.

[0010]Next, the ordinary temperature of use explains solid resin (C) by this invention. As such resin, modified phenol resin, alkyl resin, petroleum resin, polyurethane resin, etc. can be illustrated. First, as an example of modified phenol resin, rosin modified phenolic resin is mentioned and it is (1) rosin modified phenolic resin (Type 1).

Rosin modified phenolic resin produced by making carry out the pyrogenetic reaction of the phenol (and/or, substitution phenol) resin (henceforth phenol resin) resorcinized a resol type or after novolac-izing to rosin, (2) rosin modified phenolic resin (Type 2)

Rosin modified phenolic resin produced by carrying out the pyrogenetic reaction of rosin, phenol resin, and the polyhydric alcohol, (3) rosin modified phenolic resin (Type 3)

Rosin modified phenolic resin produced by carrying out the pyrogenetic reaction of rosin, phenol resin, polyvalent carboxylic acid, and the polyhydric alcohol, (4) rosin modified phenolic resin (Type 4)

Rosin modified phenolic resin produced by carrying out the pyrogenetic reaction of rosin, phenol resin, hydroxycarboxylic acid, and the polyhydric alcohol, (5) rosin modified phenolic resin (Type 5)

Rosin modified phenolic resin produced by carrying out the pyrogenetic reaction of rosin, phenol resin, petroleum resin, and the polyhydric alcohol, (6) rosin modified phenolic resin (Type 6)

At least a kind of vinylarion compound chosen from rosin, phenol resin, a vinylarion oil, vinylarion higher fatty acid, or a vinylarion alkyl resin, Rosin modified phenolic resin, such as rosin modified phenolic resin produced by carrying out the pyrogenetic reaction of the polyhydric alcohol, can be illustrated. These rosin modified phenolic resin can be independent, or can use two or more sorts together.

[0011]Here, gum rosin, wood rosin, the Indonesia rosin, tall oil rosin, disproportionation rosin, polymerization rosin, water addition rosin, etc. can be used, as rosin, these may be independent or two or more sorts of concomitant use may be sufficient as them. As phenols usable (substitution) in order to manufacture the resorcinized phenol (and/or, substitution phenol) resin a resol type or after novolac-izing, Phenol, the alkylation phenols by which the carbon

number was replaced by the straight chain of 1-20, branching, or an angular alkyl group. For example, p-cresol, m-cresol, p-propylphenol, p-isopropylphenol, p-butylphenol, p-sec-butylphenol, p-tert-butylphenol, m-tert-butylphenol, p-p-tert amylphenol, p-tert-p-tert amylphenol, p-hexylphenol, p-cyclohexylphenol, p-octylphenol, 4-(1,1,3,3-tetraethylbutyl) phenol, p-(2-ethylhexyl) phenol, p-nonyl phenol, p-decylphenol, m-decylphenol, p-dodecylphenol, m-dodecylphenol, p-undecylphenol, m-undecylphenol, p-tridecylphenol, m-tridecylphenol, p-tetradecylphenol, m-tetradecylphenol, p-pentadecylphenol, m-pentadecylphenol, p-hexadecylphenol, m-hexadecylphenol, p-heptadecylphenol, m-heptadecylphenol, 3-(1-butylhexyl) phenol, 3-(1-methylundecyl) phenol, 3-(1-methylpentadecyl) phenol, 3-(1-methylnonadecyl) phenol, 4-alpha-cumyl phenol, etc. The aryl substitution phenol in which the aromatic ring carbon number was replaced by the aryl group of 6-10. Bisphenols, such as p-phenylphenol and 4-(p-tolyl) phenol. For example, bisphenol A, the bisphenol F, the bisphenol S, tetra bromine-ized bisphenol A, etc. The phenols containing a carboxyl group, for example, salicylic acid, para-hydroxybenzoic acid, hydroxyphenyl acetic acid, hydroxyphenyl propionic acid, etc. can be illustrated. When these phenols manufacture phenol resin, they can use [ independent or ] two or more sorts together.

[0012]As a manufacturing method of phenol resin corresponding using the above-mentioned phenols here, how to carry out the pyrogenetic reaction of said phenols and the aldehyde under existence of an alkali catalyst in a drainage system or an organic solvent. Namely, after carrying out the pyrogenetic reaction of the manufacturing method or said phenols, and aldehyde of resol type phenol resin under existence of an acid catalyst in a drainage system or an organic solvent and manufacturing novolac type phenol resin first. How to obtain the phenol resin which carried out the pyrogenetic reaction and was resol-ized under existence of aldehyde and an alkali catalyst can be shown. As aldehyde used, formaldehyde, paraformaldehyde, Acetaldehyde, propionaldehyde, n-butylaldehyde, isobutylaldehyde, GURIOXI Southall, or furfural. As an alkali catalyst, sodium hydroxide, a potassium hydrate, calcium hydroxide, etc. can mention acetic acid, chloride, phosphoric acid, hypophosphorous acid, sulfuric acid, p-toluenesulfonic acid, trifluoromethyl sulfuric acid, trifluoromethyl acetic acid, etc. as an acid catalyst. A thing desirable as a degree of polymerization of the phenol resin obtained here has the preferred number of phenol nuclei from at least two or more units and a more desirable viewpoint solubles in the thing of three or more units.

[0013]With the polyhydric alcohol class used for resin modified phenolic resins of Type 2. Meen in intramolecular the compound which has two or more hydroxyls, and specifically Ethylene glycol, A diethylene glycol, triethylene glycol, a polyethylene glycol, Propylene glycol, dipropylene glycol, tripropylene glycol, A polypropylene glycol, glycerin, trimethylolmethane, trimethylolpropane, Ethoxylation trimethylolpropane, propoxy-ized trimethylolpropane. The isocyanuric acids like aliphatic series [ such as neopentyl glycol, pentaerythritol, dipentaerythritol, and sorbitol, ] type polyhydric alcohol and tri (2-hydroxyethyl) isocyanurate can be illustrated. Although the method of adding it after these polyhydric alcohol manufactures resin modified phenolic resin of Type 1, and carrying out a pyrogenetic reaction, and cheating out of an esterification reaction is generally used, it is possible for you to add at the time of resin-modified-phenolic-resin manufacture of Type 1, and to also make it

React:

[0014] Even when a reaction is catalyst-free, go on, but. Acetic acid, chloride, phosphoric acid, hypophosphorous acid, sulfuric acid, p-toluenesulfonic acid, trifluoromethyl sulfuric acid. Under acid catalyst existence, such as trifluoromethyl acetic acid, triphenyl phosphate, and triphenyl phosphite. Or tetrabutyl zirconate, a monobutyl CHINOKI side, zirconium NAFTURETO. The bottom of metal complex catalyst existence, such as tetrabutyl titanate, or magnesium oxide. It is possible to promote a reaction under existence of magnesium salt, such as magnesium hydroxide, magnesium carbonate, GCC acid magnesium, magnesium acetate, magnesium formate, and magnesium oxalate.

[0015] As polyvalent carboxylic acid which is used in manufacturing rosin modified phenolic resin of Type 3, adipic acid, maleic acid (anhydrous), fumaric acid, phthalic acid (anhydrous), itophthalic acid, terephthalic acid, trimellitic acid (anhydrous), etc. are illustrated. As hydroxycarboxylic acid which is used in manufacturing rosin modified phenolic resin of Type 4, if it is a compound which has every at least one functional group of both of hydroxyl and a carboxyl group in intramolecular, are useable. Specifically, 12-hydroxydodecanoic acid, 3-hydroxy mistake CHIRIN acid, 16-hydroxyhexadecanoic acid, 12-hydroxystearic acid, etc. can be illustrated.

[0016] With the petroleum resin which is used in manufacturing rosin modified phenolic resin of Type 5. The fraction of 20-300 \*\* of boiling points obtained in disassembly of petroleum or the case of refining is used as a starting material, it is resin manufactured by a publicly known method --- desirable --- C6 system --- petroleum resin and its carboxylic acid denaturation thing, or a cyclopentadiene. The cyclopentadiene system resin produced by carrying out thermal polymerization of the cyclopentadienes like methylcyclopentadienes and those dimers, and trimers (dicyclopentadiene etc.) (tricyclo pentadiene etc.), those carboxylic acid denaturation things, etc. can be illustrated. The carboxylic acid denaturation thing refers to what denaturalized using alphas, such as acrylic acid, maleic acid, a maleic anhydride, and maleic acid, and beta-unsaturated carboxylic acid here.

[0017] With the vinylation compound of a vinylation oil, vinylation higher fatty acid, or a vinylation alkyl resin which is used in manufacturing rosin modified phenolic resin of Type 6. After dissolving an oil, higher fatty acid, or an alkyl resin in the solvent of a hydrocarbon system if needed, what was produced by polymerizing a vinyl system monomer in the usual solution type radical polymerization method and the similar way under existence of a radical initiator is said. As a vinyl system monomer, styrene system monomers, such as styrene, vinyltoluene, and alpha-methylstyrene, are preferred. As monomers other than a styrene monomer, in addition, methyl acrylate, acrylic ester, such as ethyl acrylate, butyl acrylate, and 2-ethylhexyl acrylate. To methacrylic acid ester, such as methyl methacrylate, ethyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, and lauryl methacrylate, and a pan. The monomer which has null PORTSMITH groups, such as acrylic acid, methacrylic acid, itaconic acid, maleic acid, and a maleic anhydride, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, \*\*\*\* which has hydroxyl groups, such as 2-hydroxyethyl methacrylate and 2-hydroxypropyl methacrylate. In addition, vinyl monomers, such as glycidyl acrylate, glycidyl methacrylate, acrylamide, N-methylacrylamide, N-m-butoxy methacrylamide, N-isobutoxy methacrylamide, acrylonitrile, and vinyl acetate. can also be used.

[0018]With an oil and higher fatty acid, the oil currently generally used for the alkyl resin or the higher fatty acid is raised, and tall oil, cottonseed cake oil, soybean oil, safflower oil, drying castor oil, the linseed oil or tung oil, and these higher fatty acid are given to concrete target. In addition, as for the thing like 2 thru/or the tetramer of the linseed oil, or the polymer beyond it, the polymerized oil generally widely used for varnish-ization and a metapher are used. The alkyl resin refers to what is produced by esterifying a part for said oil or higher fatty acid, polyhydric alcohol, and polybasic acid in accordance with the process of publicly known alkyl resin. As polyhydric alcohol, glycerin, trimethylolmethane, trimethylolpropene, A diechylene glycol, neopentyl glycol, 1,6-hexanediol, DOTERAN diol, cyclohexane dimethanol, hydrogenation bisphenol A, diglycerol, polyglycerin, pentaerythritol, JIBENTA erythritol, etc. are mentioned. In addition, a bisphenol A type epoxy resin etc. can be used as polyhydric alcohol. As polybasic acid, phthalic anhydride, isophthalic acid, terephthalic acid, trimellitic anhydride, Polycarboxylic acid, such as KISANIDORO phthalic anhydride, or the ester derivative of those is mentioned adipic acid, sebacic acid, succinic acid, dodecanedioic acid, tetrahydro phthalic anhydride, monomethyl substitution tetrahydro phthalic anhydride, and monomethyl anhydrous.

[0019]Next, the resin obtained at the reaction of polyhydric alcohol and fatty acid (and/or, aromatic carboxylic acid) as alkyl resin of use by this invention. The resin obtained at the reaction of polyhydric alcohol, and an acid anhydride (and/or, polybasic acid) and polyhydric alcohol. The resin etc. which are obtained at a reaction with an acid anhydride (and/or, polybasic acid), polyhydric alcohol, and fatty acid (and/or, aromatic carboxylic acid) can show the resin at large generally expressed as alkyl resin, and limitation in particular does not have them.

[0020]as fatty acid -- saturated fatty acid, such as nonylic acid, dodecanoic acid, palmitic acid, and stearic acid, -- and, Unsaturated fatty acid, such as ricinoleic acid, oleic acid, linolic acid, linolenic acid, and elaeostearic acid, as aromatic carboxylic acid, Benzoic acid, 1-(or 2-) naphthalene carboxylic acid, etc. as polybasic acid, Fumaric acid, malonic acid, maleic acid, Malick acid, citraconic acid, itaconic acid, Adipic acid, sebacic acid, dodecanedioic acid, isophthalic acid, trimellitic acid, 2,3-(or 2,6-) naphthalene dicarboxylic acid, benzophenone tetracarboxylic acid, etc. as an acid anhydride, A maleic anhydride, anhydrous citraconic acid, itaconic acid anhydride, a succinic anhydride, A dodecanyl succinic anhydride, phthalic anhydride, trimellitic anhydride, tetrahydro phthalic anhydride, KISANIDORO phthalic anhydride etc. can be illustrated as monomethyl substitution tetrahydro phthalic anhydride and monomethyl anhydrous, and the alkyl resin of the request by blending and carrying out the pyrogenetic reaction of these at an arbitrary rate can be obtained.

[0021]Next, as petroleum resin of use, the fraction of 200-300 \*\* of boiling points obtained in disassembly of petroleum or the case of refining is used as a starting material by this invention, it is resin manufactured by a publicly known method -- desirable -- CS system -- petroleum resin and its carboxylic acid denaturation thing, or a cyclopentadiene. The cyclopentadiene system resin produced by carrying out thermal polymerization of the cyclopentadienes like methylcyclopentadienes and these dimers, and trimers (dicyclopentadiene etc.) (tricyclo pentadiene etc.), those carboxylic acid denaturation things, etc. can



be illustrated. The carboxylic acid denaturation thing refers to what denaturalized using alpha. such as acrylic acid, maleic acid, a maleic anhydride, and boletic acid, and beta-unsaturated carboxylic acid here. The petroleum modified phenol resin etc. which are produced by making acid phenols and said aldehyde react under existence of this petroleum resin can be used

[0022]Next, as a dryer (D) of use, by this invention, Acetic acid, propionic acid, butanoic acid, isopentanoic acid, hexanoic acid, 2-ethylbutanoic acid, Naphthenic acid, octylic acid, nonanoic acid, decanoic acid, 2-ethylhexanoic acid, Isocetane acid, isononanoic acid, lauryl acid, palmitic acid, stearic acid, Oleic acid, linolic acid, neo decanoic acid, BASA tic acid, seca NOIKKU acid, Telloil fatty acid, linseed-oil fatty acid, soybean oil fatty acid, dimethylhexano IKKU acid, Metal salt of organic carboxylic acid, such as 3,5,5-trimethyl hexano IKKU acid and dimethyl octanoic acid. For example, in order that it may be usable and the compound of the publicly known public use of calcium, cobalt, lead, iron, manganese, zinc, zirconium salt, etc. may promote the printer's ink surface and internal hardening, these plurality can also be used, using it together suitably.

[0023]A 1,10-phenanthroline given in JP,H4-334393,A, The manganese / acetic acid / 1,10-phenanthroline compound complex obtained at a reaction with the metal complex formed with polyvalent metal and carboxylic acid, for example, manganese acetate, and a 1,10-phenanthroline. The manganese / octylic acid / 1,10-phenanthroline compound complex obtained at the reaction of octylic acid manganese and a 1,10-phenanthroline. The manganese / naphthenic acid / 1,10-phenanthroline compound complex obtained at the reaction of manganese naphthenate and a 1,10-phenanthroline. The manganese / tall oleic acid / 1,10-phenanthroline compound complex obtained at the reaction of tall oil manganese and a 1,10-phenanthroline. The iron / naphthenic acid / 1,10-phenanthroline compound complex obtained at the reaction of naphthenic acid iron and a 1,10-phenanthroline. It is usable in the compound etc. of working example [ in the document concerned ] 1 thru/or working example 6 description of the cobalt / neo decanoic acid / 1,10-phenanthroline compound complex obtained at the reaction of neo decanoic acid cobalt and a 1,10-phenanthroline. It is also possible to encapsulate and use these dryers by the undissolved substance of the solvent of use by this invention.

[0024]Next, if it is a solvent which can dissolve acid resin at the drying oil and the ordinary temperature of use by this invention as a solvent (E) of use by this invention, there will be no limitation in particular, but it sets to use it as lithography ink, and the petroleum solvent of a high boiling point is generally used. As such a solvent, the hydrocarbon system solvent by which normal use is carried out as what is called a number solvent can be mentioned. For example, the No. 1 spindle oil made from Nippon Oil Chemicals, O item solvent L, O item solvent M, O item solvent H, the No. 4 solvent, the No. 5 solvent, initial boiling points, such as the No. 6 solvent, the No. 7 solvent, the die allene 168, and alkene 58NT, a not less than 200 \*\* petroleum solvent. An aromatic component is called the aroma free solvent made from Nippon Oil Chemicals whose initial boiling point is a not less than 200 \*\*\* petroleum solvent at 1% or less, for example, the AF solvent No. 4, the AF solvent No. 5, the AF solvent No. 6, the AF solvent No. 7, etc. are used suitably.

[0025]Next, as paints (F) of use, this invention can show an inorganic pigment and an organic color. As an inorganic pigment, the chrome yellow, zinc yellow,

Prussian blue, barium sulfate, Ked Nim Red, titanium oxide, a flower of zinc, rouge, an alumina white, calcium carbonate, ultramarine, carbon black, graphite, aluminum powder, red ochre, etc. As an organic color, As a beta-naphthol system, a beta-oxynaphthol acid system, a beta-oxynaphthol acid system Ali Lido system, Soluble azo pigment, such as an acetooacetic acid Ali Lido system and a pyrazolone system, a beta-naphthol system, A beta-oxynaphthol acid system Ali Lido system, acetooacetic acid Ali Lido system monooxo, Insoluble azo pigment, such as acetooacetic acid Ali Lido system JTSuA20 and a pyrazolone system, Copper copper phthalocyanine blue, halogenation (chlorine or bromination) copper copper phthalocyanine blue, Phthalocyanine pigment, such as sulfonation copper copper phthalocyanine blue and metal free phthalocyanine, a quinaeridone series, a dioxazine system, and the Indanthrene system (the Piren TRON and anthanthrene.) It is usable in the various points of the publicly known public use of polycyclic type paints, such as isoindolinone systems, such as indanthrene, anthra pyrimidine, flavanthrene, a thioindigo system, an anthraquinone system, a peri non system, and a perylene system, a metal complex system, and a kind PUTARON system, heterocyclic paints, etc.

[0026]To the printer's ink in this invention, it is possible to add other adjuvants if needed. As an antifriiction agent, an antiblocking agent, a slide agent, and a score-mark inhibitor, Carnauba wax, haze wax, lanolin, a monten wax, paraffin wax, Synthetic WAKKUSU, such as natural wax, such as microcrystallin wax, the Fischer FOROPUSU wax, polyethylene wax, polypropylene wax, a polytetrafluoroethylene wax, a polyamide wax, and a silicone compound, can be illustrated. As an anti-skinning agent, oxime, such as phenols, such as cresol, guaiacol, and  $\alpha$ -isopropyl phenols, and BUCHIRARUDOKISHIMU, methyl ethyl ketoxime, and cyclohexanone oxime, can be mentioned.

[0027]In a varnish, it is possible to use the gel varnish which added the gelling agent and increased the degree of cross linking of resin further. As such a gelling agent, although a metal complex is generally used, an aluminum complex compound can be mentioned as a typical compound. As such an aluminum complex compound, annular aluminum compounds. For example, annular aluminum oxide KUTETO (Kawaken Fine Chemicals: Algoma 809A), Annular aluminum oxide stearate (Kawaken Fine Chemicals: Algoma 1009S) etc., Aluminum alcoholates, for example, aluminum ethylate, aluminum isopropylate (Kawaken Fine Chemicals: AIFPD), Aluminum sec-butyrate (Kawaken Fine Chemicals: ASPD), Aluminum isopropylate mon-sec-butyrate (Kawaken Fine Chemicals: AMD) etc., Aluminum alkyl acetate (hope medicine manufacture: Chelope-AI-EN2), for example, aluminum di-n-butoxide ethylacetate. Aluminum di-n-butoxide methylacetate (hope medicine manufacture: Chelope-AI-ME2), Aluminum di-iso-butoxide methylacetate (hope medicine manufacture: Chelope-AI-MB12), aluminum di-iso-butoxide ethylacetate (hope medicine manufacture: Chelope-AI-EB102), Aluminum di-iso-PURPOKI side ethylacetate (hope medicine manufacture: Chelope-AI-EP12), Kawaken Fine Chemicals: ALCH), Aluminum \*\*\*\*-tris (ethylacetate) (Kawaken Fine Chemicals: ALCH-TR), Aluminum \*\*\*\*-tris (acetylacetate) (Kawaken Fine Chemicals: aluminum chelate A), Aluminum \*\*\*\*-\*\*\*\* (ethylacetate)-monooxetyl acetate (Kawaken Fine Chemicals: aluminum chelate D) etc., Aluminum acetylacetate, such as aluminum soap (made by Nippon Oil & Fats Co., Ltd.), for example, aluminum stearate, aluminum oleate, aluminum NAFUTENETO, and aluminum laurate, etc. can be illustrated. Normal use of these gelling agents is carried out in 0.1 to 10% of the weight of the range to varnish 100 weight

section.

[0028]The cyclic dipeptide which has the character to make oil and fat gel, as other gelling agents. For example, JP,7-247473,A, JP,7-247474,A, and cyclic dipeptide given in JP,7-247475,A. Bismide, such as ethylenebis (12-hydroxyoctadecanoic acid) AMALDO given in the bismide, for example, JP,5-320317,A, which has the character to make an organic fluid gel. The powdered aluminum magnesium compound which has a layer system given in JP,1-164432,A. For example, it is possible to use suitably an aluminum-Mg-hydroxy KAPUKI rate, aluminum-Mg-hydroxy Millis Tait, aluminum-Mg-hydroxy palmitate, aluminum-Mg-hydroxystearate, aluminum-Mg-HIDOKKI behenate, etc. [0029]The blending ratio of each ingredient which hits using the hardenable resin composition in this invention as printer's ink, as opposed to printer's ink 100 weight section of a result --- paints (F) --- 10- solid resin (C) of a solvent (E) is [ 35% of the weight of the range, and drying oil (A) / 0.1 to 10% of the weight of the range ] preferred [ at ordinary temperature / ten to 40% of the weight ] for an active oxygen generating agent (B) ten to 50% of the weight two to 35% of the weight. In actually manufacturing printer's ink, Usually, disperse composition of the paints is carried out to the varnish (and/or, gel varnish which added said gelling agent on this varnish, and was adjusted to it) by which the mixture solution of the drying oil (and ordinary temperature solid resin) may be first carried out with a solvent, and combination mixing of an active oxygen generating agent and a dryer, and the various additive agents is carried out further, and it is manufactured. For a tack and flow adjustment, drying oil or a solvent is blended further suitably, and it is manufactured.

[0030]thus, the obtained printer's ink is dried --- making --- if it hits, after printing this ink with an offset press on an impression paper (usually papers, such as art paper, coat paper, and paper of fine quality). it can attain by being exposed to actinic rays. That is, the active oxygen generating agent of use will be in an optical-pumping singlet state by exposure of actinic rays by this invention, and this excitation state changes to an excitation triplet state promptly. At this time, the energy transfer from the active oxygen generating agent of an excitation triplet state to ground state oxygen arises, and ground state oxygen turns into excitation singlet oxygen which is a kind of active oxygen promptly. This excitation singlet oxygen reacts to the unsaturation groups in the drying oil of use, resin, or an alkyd resin etc. promptly by this invention, and forms an oxide, and when an intermolecular cross linkage is promoted for this by the catalysis of a dryer, desiccation completes it.

[0031]As a source of an energy line of use, by this invention, a low pressure mercury lamp, a medium-voltage mercury-vapor lamp, A high-pressure mercury-vapor lamp, an ultrahigh pressure mercury lamp, a xenon lamp, a carbon arc lamp, a metal halide lamp, A fluorescent lamp, a tungsten lamp, an excimer lamp, an excimer laser, The source of light energy represented by various light sources, such as nitrogen laser, argon ion laser, a helium cadmium laser, helium neon laser, krypton ion laser, various semiconductor lasers, an YAG laser, a light emitting diode, a CRT light source, and a source of plasma light, is raised.

[0032]

[Function]In this invention, the active oxygen which has the character to make oxygen in a ground state excite, and this generated reacts to the carbon-carbon unsaturated bond in the constituent of this invention promptly by the exposure of actinic rays, especially optical exposure, and the active oxygen generating

agent (E) of use forms an oxide. Since it produces more promptly than the oxidation reaction by oxygen of the conventional ground state, this reaction becomes possible [ raising oxidative polymerization speed remarkably ]. On the other hand, since this active oxygen can be generated only by the optical exposure of an effective dose, it will have the character whose desiccation (set) by exposure was quick and which was excellent in preservability. Therefore, it becomes possible by using the hardenability resin composition in this invention to provide printer's ink excellent in drying property and preservability, for example, sheet offset ink, OFF ring int, offset news ink, offset-water-less version ink, etc.

[0033]

[Example]Hereafter, although this invention is made detailed in working example, this invention is not limited only below. A part shows a weight section among an example.

[0034]The example 1 (manufacture of resol type phenol resin) of manufacture After teaching 652 copies and 1506 copies of toluene, heating 2060 copies and paraformaldehyde to 60 ° and dissolving 4-((1,1,3,3-tetramethylbutyl) phenol into a stirrer, a reflux condenser, and 4 mouth flask with a thermometer, 10.3 copies of calcium hydroxide is thrown in. You made it react at 4 hours and 110 ° at 90 more ° for 2 hours, and resol type phenol resin with 4-6 average phenol-nucleus objects was obtained. It rinsed until pH was set to 6-7 after neutralization with the hydrochloric acid aqueous solution in the toluene solution of this this phenol resin. This phenol resin toluene solution is used for a reaction with the resin shown below as it is.

[0035]The example 2 (manufacture of rosin modified phenolic resin) of manufacture

In a stirrer, a reflux condenser with a mist separator, and 4 mouth flask with a thermometer, 660 copies of China gum rosin are prepared, it heats, blowing nitrogen gas, and after carrying out melting stirring and making it equalize below 260 °, you supplied 670 copies (85% of solid content) of resol type phenol resin obtained in the example 1 of manufacture, and made it react at 270 ° for 6 hours. Under the present circumstances, the reaction was made to advance while a reflux condenser with a mist separator recovered toluene and water. Subsequently, rosin modified phenolic resin (RP-1) of the acid value 16, 160 ° of resin softening temperatures, and the weight average molecular weight 80,000 was obtained by supplying 57 copies of glycerin, and 0.8 copy of p-toluenesulfonic acid, and making them react at 270 ° for 6 hours.

[0036]The example 3 (manufacture of a varnish and a gel varnish) of manufacture The rosin modified phenolic resin (A) obtained in the example 1 of manufacture was prepared [ 52 copies, 15 copies of linseed oil, and AF No. 6 solvent ] for 33 copies into 4 mouth flask, temperature up was carried out, blowing nitrogen gas, it stirred for 30 minutes at 180 °, and 100 copies of varnishes (V-1) were obtained. To the inner 55 copy of 100 copies of these varnishes, 0.6 copy of aluminum system gelling agent ALCH (Kawaken Fine Chemicals) was added, and the gel varnish (GV-1) was obtained by cooking at 180 ° for 1 hour.

[0037]27 copies and a gel varnish (GV-1) were used for working example 1 varnish (V-1). 3 rolls were used for 38 copies and six B(TOYO INK MFG. CO., LTD.) 18 copies of charge carmine of a rosy face, dispersedly. further, four copies and three copies of AF No. 6 solvents were added, and the linseed oil was distributed in a similar manner. Subsequently, 6% of manganese-naphthenate

solution (HAKIMA CHEMICALS, Inc.) was added as a dryer, three copies of benzophenones (BP) were added as G.5 copy and an active oxygen generating agent. the tack at 25 \*\* obtained 9.0 and the flow obtained the offset ink 1 of 1A.0. Immediately after [ carrying out drawdown of this ink 0.15cc to art paper with a RI tester (Akira Seisakusho Co.) 4 cut roll ], Glare for 10 seconds with the ultrahigh pressure mercury lamp of 500W, and, subsequently to, this drawdown printing is cut in the shape of a strip of paper. After pasting it together to another art paper, when time (minute) until ink stops adhering to art paper using RI tester's roll was measured and setting time was found, in the early stages of measurement, the set was already completed, namely, setting time was 0 minute. After carrying out drawdown of this ink on a glass plate by a 75-micrometer applicator, it was 9 hours when drying time (drying time on board) was investigated by finger touch every 30 minutes under the conditions of 25 \*\*/65%RH.

[0038]BP in working example 2 working example 1 was changed into four copies of diethylthio xanthenes (kaya cure DETL), and also the completely same operation as working example 1 was performed, and the offset ink 2 was obtained. The setting time of this ink was 0 minute, and drying time on board was 8 hours.

[0039]In comparative example 1 working example 1, BP was not used, and also the completely same operation as working example 1 was performed, and the offset ink 3 was created. The setting time of this ink was 15 minutes, and drying time on board was 9 hours.

[0040]

[Effect of the Invention]By using the hardenability resin composition and varnish containing the active oxygen generating agent in this invention, it becomes possible for a set to become possible [ providing the printer's ink which was quickly excellent in stability on board ], and to be able to respond to improvement in the speed of a printing machine, or to attain the slash freelaucer in sheet ink.

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(54) 【発明の名称】 硬化性樹脂組成物、ワニスならびにそれを用いた印刷インキ

(57) 【要約】

【課題】本発明の目的は、セフト性（乾燥性）および熱上安定性に優れた印刷インキを提供することにある。

【解決手段】乾性油、活性酸素発生剤、常温で固体の樹脂、さらにはドワイヤーとからなる硬化性樹脂組成物、微硬化性樹脂組成物を溶剤に溶解混合してなるワニス、さらに原料を分散混合してなる印刷インキ。

Cited document 2

(102)







キシルフェノール、p-オクチルフェノール、4-  
 (1, 1, 3, 3-テトラメチルブチル)フェノール、  
 p-(2-エチルヘキシル)フェノール、p-ニルブ  
 フェノール、p-デシルフェノール、m-デシルフェノール、  
 p-ドデシルフェノール、m-ドデシルフェノール、  
 p-ウンデシルフェノール、m-ウンデシルフェノール、  
 p-トリデシルフェノール、m-トリデシルフェノール、  
 p-テトラデシルフェノール、m-テトラデシル  
 フェノール、p-ペンタデシルフェノール、m-ペン  
 タデシルフェノール、p-ヘキサデシルフェノール、m-  
 ヘキサデシルフェノール、p-ヘプタデシルフェノール、  
 m-ヘプタデシルフェノール、3-(1-ブチル、  
 キシル)フェノール、3-(1-メチルウンデシル)フェ  
 ノール、3-(1-メチルペンタデシル)フェノール、  
 3-(1-メチルオクタデシル)フェノール、4-  
 クタデシルフェノールなど、芳香環置換数が6~10のアル  
 リール基で置換されたアリール置換フェノール、p-フ  
 ニルフェノール、4-(p-トリル)フェノールな  
 ど、ビスフェノール類、例えばビスフェノールA、ビス  
 フェノールD、ビスフェノールF、テトラブROM化ビス  
 フェノールAなど、またさらにはカルボキシル基を含有  
 するフェノール類、例えばサリチル酸、p-ヒドロキシ  
 安息香酸、ヒドロキシフェニル酸類、ヒドロキシフェニ  
 ルプロピオン酸などを例示することができる。これらの  
 フェノール類は、フェノール樹脂を製造する際に、基数  
 あるいは2種以上を併用することが可能である。

【0012】ここで、上記フェノール類を用いて相当す  
 るフェノール樹脂の製造方法としては、前記フェノール  
 類とアルデヒド類とを水系あるいは有機溶媒中でアルカ  
 リ性触媒の存在下で加熱反応する方法、すなわちレゾール  
 型フェノール樹脂の製造方法、あるいは前記フェノール  
 類とアルデヒド類とを水系あるいは有機溶媒中で酸性触  
 媒の存在下で加熱反応して先ずノラック型フェノール  
 樹脂を製造した後、アルデヒド類およびアルカリ触媒の  
 存在下で加熱反応せしめレゾール化したフェノール樹脂  
 を得る方法を示すことができる。使用されるアルデヒド  
 類としては、ホルムアルデヒド、パラホルムアルデヒ  
 ド、アセトアルデヒド、プロピオンアルデヒド、n-ブ  
 チルアルデヒド、イソブチルアルデヒド、グリオキシサ  
 ルまたはブチラールなどが、アルカリ触媒としては水  
 酸化ナトリウム、水酸化カリウム、水酸化カルシウム  
 など、酸性触媒としては硫酸、塩酸、磷酸、次亜磷酸、  
 硫酸、p-トルエンсульホン酸、トリフルオロメチル硫  
 酸、トリフルオロメチル酸などを挙げることができ  
 る。ここで得られるフェノール樹脂の重合度として好ま  
 しいものは、フェノール残基数が少なくとも2ユニット以  
 上、より好ましくは3ユニット以上のものが溶解性の観  
 点から好ましい。

【0013】タイプ2のロジン酸性フェノール樹脂に使用  
 される多価アルコール類とは、分子内にヒドロキシル

基を2つ以上有する化合物を意味し、具体的にはエチレ  
 ングリコール、ジエチレングリコール、トリエチレング  
 リコール、ポリエチレングリコール、プロピレングリコ  
 ール、ジプロピレングリコール、トリプロピレングリコ  
 ール、ポリプロピレングリコール、グリセリン、トリメ  
 チロールエタン、トリメチロールプロパン、エトキシ化  
 トリメチロールプロパン、プロポキシ化トリメチロール  
 プロパン、ネオペンテリグリコール、ペンタエリスリト  
 ール、ジペンタエリスリトール、ソルビトールなどの脂肪  
 族型の多価アルコール、トリス(2-ヒドロキシエチル)  
 イソシアヌレートのごときイソシアヌレート類を例示  
 することができる。これら多価アルコールは、タイプ1  
 のロジン酸性フェノール樹脂を製造した後に添加し、加  
 熱反応させエステル化反応をせしめる方法が一般的に用  
 いられるが、タイプ1のロジン酸性フェノール樹脂製造  
 時に添加し反応せしめることも可能である。

【0014】反応は触媒フリーでも進行するが、触媒、  
 塩酸、硫酸、次亜硫酸、硫酸、p-トルエンсульホン  
 酸、トリフルオロメチル硫酸、トリフルオロメチル硫  
 酸、トリフェニルホスファート、トリフェニルホスファ  
 イトなどの酸触媒存在下、あるいはテトラブチルコ  
 ーホート、モノブチルチンコサイド、ジブチルチンコ  
 テネート、テトラブチルチンコサートなどの金属錯体触媒  
 存在下、あるいは酸化マグネシウム、水酸化マグネシウ  
 ム、炭酸マグネシウム、炭酸カルシウム、酢酸マグ  
 ネシウム、硫酸マグネシウム、および硫酸マグネシウム  
 などのマグネシウム塩類などの存在下において反応を促  
 進させることが可能である。

【0015】タイプ3のロジン酸性フェノール樹脂を製  
 造するに当たって使用される多価カルボン酸類として、  
 アジピン酸、(無水)マレイン酸、ママ酸、(無水)  
 フタル酸、イソフタル酸、テレフタル酸、(無水)ト  
 リメリット酸などが例示される。タイプ4のロジン酸  
 性フェノール樹脂を製造するに当たって使用されるヒド  
 ロキシカルボン酸としては、分子内にヒドロキシル基と  
 カルボキシル基の両官能基を少なくとも1つ含有する  
 化合物であれば使用可能で、具体的には1,2-ヒドロキ  
 シドデカノ酸、3-ヒドロキシミステラン酸、1,5-ヒ  
 ドロキシヘキサデカノ酸、1,2-ヒドロキシステアリン  
 酸などを例示することができる。

【0016】タイプ5のロジン酸性フェノール樹脂を製  
 造するに当たって使用される石油樹脂とは、石油の分  
 割または改質の際に得られる沸点260~300℃の留分  
 を出発原料として、分留の方法で製造される樹脂であり、  
 好ましくは0.3%石油樹脂およびそのカルボン酸(酸性物  
 あるいはシクロペンタジエン、メチルシクロペンタジ  
 エン及びこれらの二量体(ジシクロペンタジエンなど)、  
 三量体(トリシクロペンタジエンなど)のごときシクロ  
 ペンタジエン類を熱重合して得られるシクロペンタジ  
 エン系樹脂およびそれらのカルボン酸酸性物などが例示で

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まる。ここでカルゲン酸炭性物とは、アクリル酸、マレイン酸、無水マレイン酸、フマル酸などの $\alpha$ 、 $\beta$ -不飽和カルゲン酸を用いて変性したものをいう。

【0017】タイプBのロジン変性フエノール樹脂を製造するに当たって使用されるビニル化合物、ビニル化高凝脂脂肪酸またはビニル化アルキッド樹脂のビニル化合物としては、油、高凝脂脂肪酸またはアルキッド樹脂を必要に応じて炭化水素の溶剤に溶解したのち、ラジカル開始剤の存在下に通常の溶液ラジカル重合法と同様の方法にて、ビニル系単量体を重合して得られるものを用いる。ビニル系単量体としては、スチレン、ビニルトルエン、 $\alpha$ -メチルスチレンなどのスチレン系単量体が好ましい。

その他、スチレン系単量体以外の単量体としてはメチルアクリレート、エチルアクリレート、ブチルアクリレート、2-エチルヘキシルアクリレート等のアクリル酸エステル類、メチルメタクリレート、エチルメタクリレート、ブチルメタクリレート、2-エチルヘキシルメタクリレート、オクチルメタクリレート等のメタクリル酸エステル類、さらには、アクリル酸、メタクリル酸、イタロン酸、マレイン酸、無水マレイン酸等のカルギン系を有する単量体、2-ビドロキシエチルアクリレート、2-ビドロキシプロピルアクリレート、2-ビドロキシエチルメタクリレート、2-ビドロキシプロピルメタクリレート等の水溶性を有する単量体、その他、グリセロールアクリレート、グリセロールメタクリレート、アクリルアミド、N-メダロールアクリルアミド、N-イソプロピルアクリルアミド、アクリルアミド、アクリロニトリル、酢酸ビニル等のビニル単量体も使用しうる。

【0018】油、高凝脂脂肪酸とは、一般にアルキッド樹脂に使用されている油またはその高凝脂脂肪酸があげられ、具体的に1-油、種菜油、大豆油、サフラワー油、脱水和マリン油、アマニ油または桐油およびこれらの高凝脂脂肪酸があげられる。この他に一般にフニク化によく用いられる重油、たとえばアマニ油の2ないし4量体またはそれ以上の重合体のごときものも使用される。また、アルキッド樹脂とは前記油または高凝脂脂肪酸分、多価アルコール、多価炭素を公知のアルキッド樹脂の製法に従いエステル化して得られるものをいう。多価アルコールとしては、グリセリン、トリメチロールエタン、トリメチロールプロパン、ジエチレングリコール、ネオペンタグリコール、1,6-ヘキサングリコール、ドデカニール、シクロヘキサングリコール、水添ビスフェノールA、ジグリセリン、ポリグリセリン、パンタエリスリトール、ジペンタエリスリトール等が挙げられる。

また、その他にビスフェノールA型エポキシ樹脂等も多価アルコールとして使用しうる。多価炭素として無水フタル酸、イソフタル酸、テレフタル酸、無水トリメリット酸、アジピン酸、セバチン酸、コハク酸、ドデカニール酸、テトラビドロ無水フタル酸、モノメチル炭素テトラ

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ビドロ無水フタル酸、モノメチル無水ヘキサビドロ無水フタル酸等のポリカルボン酸類またはそのエステル誘導体等が挙げられる。

【0019】次に本発明で使用するアルキッド樹脂としては、多価アルコールと脂肪酸（および/または芳香族カルボン酸）との反応で得られる炭酸、多価アルコール、炭酸無水物（および/または多価炭素）と多価アルコールとの反応で得られる樹脂、炭酸無水物（および/または多価炭素）、多価アルコールおよび脂肪酸（および/または芳香族カルボン酸）との反応で得られる樹脂など、一般的にアルキッド樹脂と表される樹脂全般を示すことができるに限定されない。

【0020】脂肪酸としては、ノニル酸、ドデカニール酸、パルミチン酸、ステアリン酸などの飽和脂肪酸および、リノール酸、オレイン酸、リノール酸、リノレン酸、エリコステリン酸などの不飽和脂肪酸を、芳香族カルボン酸としては、安息香酸、1-（または2-）ナフトレンカルボン酸などを、多価炭素としては、フマル酸、マロン酸、マレイン酸、マリン酸、シクロコン酸、イタコン酸、アジピン酸、セバチン酸、ドデカニール酸、イソフタル酸、トリメリット酸、2,3-（または2,6-）ナフトレンジカルボン酸、ベンゾフェノントラカルボン酸などを、炭酸無水物としては、無水マレイン酸、無水シクロコン酸、無水イソコン酸、無水コハク酸、ドデセニル無水コハク酸、無水アタクミ酸、無水トリメリット酸、テトラビドロ無水フタル酸、モノメチル炭素テトラビドロ無水フタル酸、モノメチル炭素ヘキサビドロ無水フタル酸などを例示することができ、これらを任意の割合で配合し加熱反応せしめることにより所望のアルキッド樹脂を得ることができる。

【0021】次に本発明で使用する石油樹脂としては、石油の分餾または改質の際に得られる沸点200〜300℃の留分を出発原料として、公知の方法で製造される樹脂であり、好ましくはC5系石油樹脂およびそのカルゲン酸炭性物あるいはシクロペンタジエン、メチルシクロペンタジエン及びこれらの二量体（ジシクロペンタジエンなど）、三量体（トリシクロペンタジエンなど）のごときシクロペンタジエン類を重合して得られるシクロペンタジエン系樹脂およびそれらのカルボン酸炭性物などが例示できる。ここでカルゲン酸炭性物とは、アクリル酸、マレイン酸、無水マレイン酸、フマル酸などの $\alpha$ 、 $\beta$ -不飽和カルゲン酸を用いて変性したものをいう。

また、炭石樹脂の存在下に、炭記フェノール類および炭記アルデヒド類とを反応させて得られる石油変性フェノール樹脂なども使用することができる。

【0022】次に本発明で使用するダイマー（D）としては、酢酸、プロピオン酸、酪酸、イソブタン酸、ヘキサン酸、2-エチル酪酸、ナフテン酸、オクタノール、ノナン酸、デカン酸、2-エチルヘキサン酸、イソオクタノール、イソノナン酸、ラウリン酸、パルミチン酸、テ

【0025】次に本発明で使用する原料（下）としては、無機原料および有機原料を示すことができる。無機原料としては炭素、珪素、酸素、窒素、硫黄、リン、カリウム、

【0027】また炭素にワニスに依りては、ゲル化反応を  
 添加し樹脂の弾性をさらに増進したゲルワニスを使用す  
 ることが可能である。その様なゲル化剤としては、一  
 般的には金属塩類が用いられるが、代官的な化合物とし  
 てアルミニウム錯体化合物を挙げることができる。その  
 様なアルミニウム錯体化合物としては、環状アルミニウ  
 ム化合物を、例えば環状アルミニウムオキサイドオク  
 45 トラート（用語：ファインケミカル：ALGマーク-800A）、  
 環状アルミニウムオキサイドステアラート（用語：ファイン  
 ケミカル：アルマーク-1600CS）など、アルミニウム  
 アルコキシド類、樹木は、アルミニウムエーテル、  
 アルミニウムイソプロピレート（用語：ファインケミ  
 50 ル：A1FD）、アルミニウム-シェンアチレート  
 （用語：ファインケミカル：ASPD）、アルミニウムイ  
 ソプロピレート-モノ-エーテルブチレート（用語：ファ  
 インケミカル：AMD）など、アルミニウムアルキル  
 シェンアチド類、例えばアルミニウム-ジ（ブチル）ア  
 シンアチド類、アルミニウム-ジ（ブチル）アチンアチド

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ジエチルアセトアセテート（ホープ製薬：Chelopac-A1-EB2）、アルミニウムジエチルアセトアセテート（ホープ製薬：Chelopac-A1-MB2）、アルミニウムジエチルアセトアセテート（ホープ製薬：Chelopac-A1-MB12）、アルミニウムジエチルアセトアセテート（ホープ製薬：Chelopac-A1-EB162）、アルミニウムジエチルアセトアセテート（ホープ製薬：Chelopac-A1-EB12）、川崎フライングミカル（ALCH）、アルミウムトリエチルアセトアセテート（川崎フライングミカル：ALCH-TB）、アルミウムトリエチルアセトアセテート（日本油研（株））、アルミニウムオレエチル、アルミニウムナフテネート、アルミニウムラウレートなど、およびアルミニウムアセチルアセトアセテートなどを例示することができる。これらのゲル化剤は、重量100重量部に對し、5.1重量%から10重量%の範囲で適量使用される。

【0028】また、その他のゲル化剤として、油類類をゲル化せしめる性質を有するジブチルアセテート、例えば特開平7-247473、特開平7-247474および特開平7-247475に記載の環状ジブチルアセテート、有機酸体をゲル化せしめる性質を有するビスアミド類、例えば特開平5-320617に記載のエチレンビス（1,2-エチドキシシタタカン）アミドなどのビスアミド類、特開平1-164432記載の環状構造を有する輪状のアルミニウム-マグネシウム化合物、例えばAl-Mg-ヒドロキシシリケート、Al-Mg-ヒドロキシナフテネート、Al-Mg-ヒドロキシステアレート、Al-Mg-ヒドロキシパルメイトなどを適量使用することが可能である。

【0029】本発明における酸化性脂質組成物を、印刷インキとして使用するに当たっての各成分の配合割合は、仕上りの印刷インキ100重量部に對し、顔料（F）が10〜35重量%の範囲、乾性油（A）が2〜35重量%、樹脂（B）が10〜50重量%、常温で固体の樹脂（C）が10〜40重量%、活性酸素発生剤（E）が0.1〜10重量%の範囲が好適である。また、印刷インキを樹脂に製造するに際しては、適量または乾性油（および常温で固体の樹脂）を溶剤によって混合溶解せしめ得られるワニス（および/または該ワニスを原料にゲル化剤を添加して調製されたゲルワニス）に原料を分散配合し、さらに活性酸素発生剤およびドライヤー、各種添加剤を配合混合し製造される。またタックオフ

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およびアロー調整のために、さらに乾性油あるいは樹脂を適量配合し製造される。

【0030】この係にして得られる印刷インキを乾燥せしめるに当たっては、該インキを例えばオフセット印刷版にて被印刷体（被塗布体）に塗布し、上質紙などの紙）上に印刷した後、活性油に暴露することにより達成される。すなわち、本発明で使用する脂質組成物発生剤が活性油の暴露により光硬化一重項状態となり、微動状態は速やかに励起三重項状態に遷移する。この時、励起三重項状態の活性酸素発生剤から基底状態酸素のエネルギー移動が生じ、基底状態酸素は速やかに活性酸素の一種である励起一重項酸素となる。この励起一重項酸素は、本発明で使用する乾性油中、ロジエン中、あるいはアルキッド樹脂中などの不飽和基と速やかに反応し酸化物を形成し、これがドライヤーの乾燥作用によって分子間架橋が促進されることにより乾燥が完了する。

【0031】本発明で使用するエネルギー源としては、紫外線光源、中波紫外線灯、高圧水銀灯、超高圧水銀灯、キセノンランプ、カーボンアーク灯、メタルハライドランプ、蛍光灯、タングステンランプ、エキシマランプ、エキシマレーザー、窒素レーザー、アルゴンイオンレーザー、ヘリウムカドミウムレーザー、ヘリウムネオンレーザー、クリプトンイオンレーザー、各種半導体レーザー、YAGレーザー、発光ダイオード、CR光源、ラザルス光源等の各種光源に代換をされる光エネルギー源があげられる。

【0032】

【作用】本発明において使用する活性酸素発生剤（E）は、活性油の照射、特に光照射により、基底状態にある酸素を励起せしめる性質を有し、これにより発生した活性酸素は、本発明の組成物中の成膜一成分不飽和基と速やかに反応し酸化物を形成する。この反応は、従来の基底状態の酸素による酸化反応より速やかに進むため、酸化重合速度を著しく高めることが可能となる。一方、該活性酸素は、有効量の光照射によってのみ発生させることが可能であるため、照射による乾性（セッ）は速く、且つ保存性には優れた性質を有することとなる。したがって、本発明における酸化性脂質組成物を用いることによって、乾性速く且つ保存性に優れた印刷インキ、例えば、乾性オフセットインキ、オフセットオフセット印刷インキ、オフセット水無し印刷インキなどを提供することが可能となる。

【0033】

【実施例】以下、実施例にて本発明を詳細にするが、本発明は下記のみに限定されるものではない。尚、割合、部は重量部を示す。

【0034】製造例1（レゾール型フェノール樹脂の製造）

攪拌器、還流冷却器、温度計付きの4口フラスコ中に、4-（1, 1, 3, 3-テトラメチルプロピル）フッ

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ノールを2060部と、パラホルムアルサヒドを652部と、1ルエンを1500部を注込み、60℃まで加熱し溶解した後、水酸化カルシウムを10、3部投入する。さらに90℃で4時間と110℃で2時間反応せしめ、平均フェノール単位数4～6のレゾールを型フェノール樹脂を得た。この型フェノール樹脂のトルエン溶液を塩酸水溶液で中和後、pHが6～7になるまで水洗を行った。該フェノール樹脂トルエン濃度は、以下に示すロジンとの反応にそのまま使用する。

【0035】製造例2（ロジン酸性フェノール樹脂の製造）

脱酸器、水分離器付き還流冷却器、温度計付きの4つ口フラスコ中に、中圧ガムロジン680部を注込み、酸素ガスを吹き込みながら加熱し、200℃以下で溶融機押し均一化せしめた後、製造例1にて得られたレゾール系フェノール樹脂670部（固形分65%）を投入し270℃で6時間反応せしめた。この際、トルエンと水を水分離器付き還流冷却器で回収しながら反応を進行せしめた。次いで、グリセリン57部とポर्टルエンスルホン酸を9、3部投入し70℃で6時間反応せしめることにより酸価16、樹脂軟化点160℃、重量平均分子量8万のロジン酸性フェノール樹脂（R-P-1）を得た。

【0036】製造例3（ブニスおよびゲルワニスの製造）

製造例1にて得たロジン酸性フェノール樹脂（A）を52部、アミノ油15部、AF6号ソルベントを33部を4つ口フラスコ中に注込み、酸素ガスを吹き込みながら昇温し、180℃で30分間攪拌しワニス（V-1）を100部得た。該ワニス100部の内50部に、アルミニウム系ゲル化剤ALCH（川研ファインケミカル）を0、6部添加し、180℃で1時間クッキングすることによりゲルワニス（GV-1）を得た。

【0037】実施例1

ワニス（V-1）を37部、ゲルワニス（GV-1）を32部、紅顏料カーミン6B（電研インキ製造（株）

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18部を三本ロールを用いて分岐し、さらにアマニ油を4部、AF6号ソルベントを3部を加え開線に分散した。次いで、ドライマーとして6%のナフチン酸マンガン溶液（ハリマ化成（株））を0、5部、塩化亜鉛塩基剤としてペンゾフェノン（B-P）を3部加え、25℃におけるクッキングが0、ワローが18、0のオフセットインキ-1を得た。該インキ0、15ccをR1スター（（株）明製作研）4カットロールでアート紙に染色した直後、500Wの超高圧水銀灯にて1秒照射し、次いで該染色刷りを乾燥状態に切り、それを別のアート紙に貼り合わせた後、R1スターのロールを用いてインキがアート紙に付着しないまでの時間（分）を測定し、セット時間を求めたところ、測定初期において既にセットが終了しており、すなわちセット時間は0分であった。また、該インキを25μmのフロッグクターでガラス板上に染色したのも、25℃/65%RHの条件下で30分間に乾燥乾燥時間（鏡上乾燥時間）を測定したところ8時間であった。

【0038】実施例2

実施例1におけるB-Pをジエチルチオキサンテン（カヤキエーアドエス）4部に換えた他は、実施例1と全く同様の操作を行い、オフセットインキ-2を得た。該インキのセット時間は0分、鏡上乾燥時間は8時間であった。

【0039】比較例1

実施例1において、B-Pを用いない他は実施例1と全く同様の操作を行いオフセットインキ-3を作成した。該インキのセット時間は15分、鏡上乾燥時間は9時間であった。

【0040】

【発明の効果】本発明における活性酸素発生剤を含有する硬化性樹脂組成物およびワニスをを用いることにより、セットが速く且つ鏡上安定性に優れた印刷インキを達成することが可能となり、印刷機の高速化に対応でき、あるいは改進黨インキにおけるスターチフリーを達成することが可能となる。